To get a clear idea about the nature of errors, let us denote

$$l_{1,r} \equiv \frac{\partial}{\partial r} + \frac{2}{r}, \; l'_{1,r} \equiv \frac{\partial}{\partial r} + \frac{1}{r}, \qquad \ldots(8)$$

$$l_{2,r} \equiv \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} - \frac{4}{r^2}, \quad l'_{2,r} \equiv \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} - \frac{1}{r^2}. \qquad \ldots(9)$$

The linear operators are defined on a set of functions having continuous derivative of the second order in $[a, b]$ which, after topologising in the usual way, is denoted by $D_2[a,b]$ (Shilov, 1965). It is easy to see that

$$l_{2,r} \equiv \left(l_{1,r} - \frac{3}{r}\right), \; l'_{1,r} \equiv \left(l'_{1,r} - \frac{1}{r}\right) l'_{1,r} \qquad \ldots(10)$$

Relations (10) show that the solutions of $l_{1,r}\, u = 0$ and $l_{1,r}\, u = 0$ are solutions of $l_{2,r}\, u = 0$ and $l'_{2,r}\, u = 0$, respectively. But the converse is not true. Nonnull images of the set points in $D_2[a, b]$ for which $\left(l_{1,r} - \frac{3}{r}\right)u = 0$ and $\left(l'_{1,r} - \frac{1}{r}\right) u = 0$, respectively, with respect to $(l_{1,r})^{-1}$ and $(l'_{1,r})^{-1}$ are solutions of $l_{2,r}\, u = 0$, and $l'_{2,r}\, u = 0$, respectively, but evidently $l_{1,r}\, u \neq 0$ and $l'_{1,r}\, u \neq 0$.

References

Chatterjee, D. 1968 *Indian J. Phys.* **42**, 539.

Cinelli, G. 1965 *Intern Jour. Eng. Sciences* **3**, 539.

Cinelli, G. 1966 *Jour. Appl. Math.*, 825.

Dutta, M. & Debnath, L. 1965 *Stud. Univ. Bab.* 33, 37.

Love, A.R.H. 1944 *On the Mathematical Theory of Elasticity*, Dover Publication, N.Y.

Shilov, G. Ye. 1965 *Mathematical Analysis*, Pergamon Press, Oxford

Indian J. Phys. 34, 705—707 (1969)

Decay characteristics of CaS (Zr, Di) phosphors

By B. R. Malhotra

Central Road Research Institute, New Delhi.

(Received 22 August—Revised 23 December 1969)

Phosphorescence decay characteristics of CaS phosphors activated with Zr and Di (Pr+Nd) impurities have been studied to gather information about the type of phosphorescence decay, value of time constant of decay and the effective trap depths contributing to the phosphorescence in this system of phosphors.

Experimental results reveal that decay of phosphorescence follows the hyperbolic relation $I = I_0 . t^{-b}$ with b varying from 0.77 to 0.92 and the kinetics being monomolecular. The value of decay constant b increases with the increase in concentration of Di impurity implying thereby that Di atoms introduce shallow traps which get emptied soon. Group of traps with trap depth 0.7 ev contribute most effectively to the phosphorescence. The close agreement between two values of trap depths E as obtained from phosphorescence decay and thermoluminescence justifies the validity of the fundamental equation $p = s . e^{-E/kT}$ in this system of phosphors.

Blokhinsev (1937) and De Groot (1939) were the first among early workers who derived a theoretical time dependence of the decay of phosphorescence from considerations of electron transitions between various energy levels. Lord *et al* (1947) identified these energy states as arising activators which have lost their electrons. The decay of phosphorescence is distinguished to be of two types depending on whether the kinetics involved in the luminescence process are of the first order or of the second order. Radiative transitions which are monomolecular in character, result in exponential decay of the form $I = I_0 . \exp(-pt)$, while in the case of bimolecular mechanism involving recombination of the free electrons and holes, the decay obeys the inverse square law, $I = I_0/(1+\alpha t)^2$.

Phosphorescence decay charscteristics of CaS phosphors activated with zirconium and rare earth didymium (praesodymium+neodymium) have been studied to gather information on the type of decay and trap depths contributing to phosphorescence. Phosphors were prepared by heating an intimate mixture of $CaSO_4$, a triple flux, activators zirconium and didymium in suitable proportions at 950°C for two hours in a reducing atmosphere of carbon. Four series of phosphors with different constant concentrations of Zr in respective series were prepared and didymium content was varied from .001 to 0.4 percent by weight of $CaSO_4$ in each series.

Decay characteristics were studied by plotting intensity measured in arbitrary units against time on logarithmic scale. The deviation of the curve from the straight line eliminates the possibility of exponential decay. However the $\log I - \log t$ curve shows a linear relationship signifying a hyperbolic decay of the $I = I_0 . t^b$ where b is known as decay constant. The hyperbolic decay is supposed to result from the superposition of intensities, each of which is varying exponentially with time, when different trap depths are involved in contributing to phosphorescence. The decay constant b has been calculated by introducing new variables to get a more workable relationship. So taking the logarithm of the above expression,

$$\log I = \log I_0 + b \log t$$

and putting $y = \log I$, $x = \log t$ and $c = \log I_0$,

we get, $y = bx + c$

The problem is simplified to, fitting a straight line to a set of points in the xy plane and thus to a simple problem of least squares. b and c can be calculated from the following expressions :

$$b = \frac{\Sigma x . \Sigma y - n\Sigma xy}{(\Sigma x)^2 - n\Sigma x^2}$$

$$c = \frac{\Sigma y . \Sigma x^2 - \Sigma x . \Sigma y}{n\Sigma x^2 - (\Sigma x)^2}$$

Value of b has been calculated for all the samples in the time interval from 5 seconds after excitation to the time when the intensity decayed to a negligibly small value. As b turns out to be a negative quantity, the equation becomes $I = I_0 . t^{-b}$.

As shown by data collected for all the samples, value of decay constant varies from 0·77 to 0.92 with the increase in concentration of Di which implies that Di introduces shallow traps which get emptied soon, thus giving a higher value of the decay constant. Hyperbolic decay is considered to be the result of superposition of exponentials corresponding to different trap depths. To determine the different traps contributing to phosphorescence, the decay curves were broken into three exponentials and trap depths corresponding to these were determined. Trap depths as calculated from the three exponentials for most of the phosphors are 0.61, 0.65 and 0.69 ev From the limited number of exponentials it is reasonable to assume the distribution to be Gaussian. Thus the group of traps contributing predominantly to phosphorescence may be assigned the value of trap depth corresponding to that of its maximum, i.e. 0·69. This value of trap depth is in close agreement with that determined from glow-curve experiment implying thereby that the kinetics involved are mono-molecular and the validity of the equation $p = s.e^{-E/kT}$ holds good.

References

Blokhinsev D. 1937 *J. Exptl. Theor Physics. U.S.S.R.* 7, 1242.

De Groot W. 1949 *Phys.* 6, 275.

Lord, Rees & Wise 1947 *Proc. Phys Soc.* 59, 488.